

PATENT SPECIFICATION

Inventor: LEO PHILIPP ELLINGER



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COMPLETE SPECIFICATION

Improvements in or relating to Catalysts

We, THE BRITISH OXYGEN COMPANY LIMITED, a British company, of Bridgewater House, Cleveland Row, St. James's, London, S.W.1, do hereby declare this invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to catalysts and relates more particularly to copper acetylide catalysts for the reaction between acetylene and formaldehyde to form 2-butyne-1:4-diol.

2-butyne-1:4-diol (hereinafter referred to as butynediol) is usually prepared by reacting acetylene with an aqueous solution of formaldehyde in the presence of a catalyst consisting essentially of copper acetylide. The catalyst can be prepared by reacting an aqueous solution of a copper salt with acetylene under appropriate conditions, removing the precipitated copper acetylide and transferring it to the vessel in which the acetylene and the formaldehyde are to be reacted. This procedure may give rise to difficulties in handling the free copper acetylide (which can decompose explosively when dry) and, moreover, it has been found that the catalyst particles are liable to attrition during the course of reaction, so that difficulties arise in separating the catalyst and the product liquor.

To obtain a more robust catalyst, it has been proposed to support the catalyst on a porous solid medium, the procedure being to deposit the copper salt on the support and to convert it to copper acetylide *in situ*. A preferred support has been silica gel, and in order to obtain a satisfactory catalyst, it has been necessary for the catalyst support to be specially prepared. Catalysts have been described in which the amount of copper held on the support was 10—12% by weight.

It is an object of the present invention to provide a catalyst much richer in copper than such silica gel-supported catalysts, but which is nevertheless robust and free from the disadvantages of the unsupported catalyst.

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It is a further object of the invention to provide a simplified procedure for the preparation of such a catalyst.

Yet a further object of the invention is to provide a catalyst which is more efficient on overall considerations.

According to the present invention, a process for the preparation of a catalyst capable of catalysing the reaction between acetylene and formaldehyde to form 2-butyne-1:4-diol, comprises as a first stage the preparation of a copper silicate material containing 15—60% by weight of copper, by mixing the requisite proportions of a solution of a copper salt and a solution of an alkali metal silicate, the copper silicate material being subsequently treated with acetylene, to convert the copper content of the material to copper acetylide.

The copper silicate may be separated, washed, and dried by heating in air to temperatures up to 500° C. or above, or by warming to only slightly elevated temperatures under reduced pressure. On drying it forms cakes which can readily be broken into granules, but the invention is not limited to the use of such material. For example, the material may be extruded into rods or converted into other suitable forms prior to drying. It can, if desired, be mixed with materials inert in respect to the reaction between acetylene and formaldehyde such as kaolin prior to drying, and then pelleted. If the material is heated above about 100° C. in the drying process, its colour may change from light blue to black, but catalysts can be prepared from either the blue or the black material.

It is possible, if desired, to impregnate the copper silicate material with further amounts of copper by immersion in a solution of a copper salt and subsequent ignition. In this way, the copper content of the final material can be raised, but this is not essential for the preparation of a useful catalyst.

It is possible to convert the precipitated copper silicate into a copper acetylide catalyst without prior separation from its mother

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liquor, but this is not a preferred method of operating the process of our invention.

It is sometimes considered desirable to incorporate in the catalyst for the reaction between acetylene and formaldehyde other materials, generally described as "cuprene inhibitors". A particularly useful example of such inhibitors is bismuth. In carrying out the process of the present invention it is possible to incorporate bismuth or other such inhibitors in the catalyst, either during the first stage of precipitating the copper silicate material or by immersing the dry copper silicate granules in an appropriate solution. It has, however, been found that cuprene formation is greatly reduced when catalysts prepared in accordance with the present invention are used as compared with unsupported or silica gel-supported catalysts, and the use of such cuprene inhibitors is accordingly unnecessary.

The copper silicate material may be converted into the actual catalyst used in the reaction by suspending it in water and treating with acetylene, the wet material subsequently being transferred to the reactor in which the reaction between acetylene and formaldehyde is to be effected. Alternatively and preferably the conversion may be carried out *in situ* in the reactor; in this case, the copper silicate material is added to the aqueous formaldehyde which is warmed above 60° C. and acetylene is then fed to it. The catalyst so prepared is robust. In batch processes in which the catalyst is suspended in aqueous formaldehyde and the latter reacted with acetylene under pressure, the product liquor subsequently being separated from the catalyst which is then re-used, the catalyst of the present invention can be used repeatedly for a large number of successive operations. The separation of product liquor and catalyst remains facile even after much repeated use of the same batch of catalyst. In continuous operation in which aqueous formaldehyde and acetylene are each flowed through a bed of catalyst, catalysts prepared according to the present invention are much less subject to attrition, to dislodgement of copper acetylide, or to blockages causing resistance to flow than are either unsupported copper acetylide or copper acetylide supported on pre-prepared supports.

It is a further advantage of catalysts prepared in accordance with the present invention that a given amount of such a catalyst is capable of catalysing the reaction between acetylene and formaldehyde to a greater extent than the same amount of supported catalyst.

The invention is illustrated by the following examples:—

EXAMPLE 1.

An aqueous solution containing 140 g. of copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) was added to an excess of an aqueous solution of waterglass (30% $\text{Na}_2\text{Si}_2\text{O}_5$) with stirring and the precipitate was filtered, washed with distilled water

and dried at 80° C. The product contained 23.5% by weight of copper. It was heated to 220° C. cooled and immersed for 20 minutes in an aqueous solution containing 305 g. per litre of copper nitrate and 46 g. per litre of bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$). The product was filtered, dried at 220° C. and was roasted at 500° C. until it no longer fumed. 150 g. of a black powder containing 41.2% by weight of copper and 11.7% by weight of bismuth were obtained.

125 g. of a black powder prepared as above were placed in a 1 litre autoclave together with 540 g. of a 42.6% (by weight) solution of formaldehyde. After venting with nitrogen, acetylene was admitted at 20 atms. and 80° C. and during $\frac{1}{2}$ hour, while the acetylide catalyst was formed, the temperature was raised to 100° C. Acetylene absorption ceased after 7 hours. During this period, 126 g. of acetylene was absorbed.

The product was filtered from the catalyst. It was found to contain 41.6% by weight of butynediol, 10.1% of propargyl alcohol and 0.5% of formaldehyde.

The same catalyst was re-used, using 440 g. of a 52.3% (by weight) solution of formaldehyde, 200 g. of water and acetylene at 20 atms. and 100° C. During 5 hours 110 g. of acetylene was absorbed. The product was filtered and the resulting solution contained 300 g. of butynediol (56.8% by weight), 31 g. of propargyl alcohol (6%), and 3.5 g. of formaldehyde (0.7%). The yield of butynediol on formaldehyde was 91% and that of propargyl alcohol 7%.

This procedure was repeated nine times without any slowing of the reaction, deterioration in the quality of the product, or excessive difficulty in the filtration of the reaction product from the catalyst.

EXAMPLE 2.

Aqueous solutions of 30% waterglass (1.73 kg.) and of copper nitrate (363 g.) were mixed and the resulting precipitate washed and roasted at 220° C. The product contained 55.2% of copper.

65 g. of this material was used in the preparation of the acetylide and a similar procedure was followed to that of Example 1. Almost identical results were obtained.

EXAMPLE 3.

Copper silicate was prepared as in Example 2, but instead of the roasting at 220° C., it was heated at 120° C. for 8 hours before being converted to copper acetylene and used in the acetylene-formaldehyde reaction. In operation this catalyst gave results substantially similar to those of Example 1.

What we claim is:—

1. Process for preparation of a catalyst capable of catalysing the reaction between acetylene and formaldehyde to form 2-butyne-1:4-

- diol comprising as a first stage, preparing a copper silicate material containing 15—60% by weight of copper by mixing the requisite proportions of a solution of a copper salt, and a solution of an alkali metal silicate, and subsequently treating the copper silicate material with acetylene to convert the copper content of said material to copper acetylide.
2. Process according to Claim 1, wherein the copper silicate material is separated, washed and dried prior to its treatment with acetylene.
3. Process according to Claim 2, wherein the copper silicate material is extruded into rods, pelleted, or converted into other suitable forms, prior to drying.
4. Process according to Claim 3, wherein the copper silicate material is mixed with material inert in respect to the reaction between acetylene and formaldehyde.
5. Process according to any of Claims 2 to 4, wherein the copper silicate material is impregnated with a further amount of copper prior to its treatment with acetylene.
6. Process according to any of the preceding claims, wherein a cuprene inhibitor is incorporated in the catalyst.
7. Process according to any of the preceding claims, wherein the conversion of the copper silicate material to the catalyst is effected by suspending the copper silicate material in water and treating it with acetylene.
8. Process according to any of Claims 1 to 6, wherein the conversion of the copper silicate material to the catalyst is effected by suspending the copper silicate material in aqueous formaldehyde and heating it with acetylene at a temperature above 60° C.
9. Process for the preparation of a catalyst capable of catalysing the reaction between acetylene and formaldehyde to form 2-butyne-1:4-diol substantially as hereinbefore described with reference to any of Examples 1 to 3.
10. A catalyst capable of catalysing the reaction between acetylene and formaldehyde to form 2-butyne-1:4-diol, when prepared by the process of any of Claims 1 to 9.
11. The method of preparing 2-butyne-1:4-diol by reaction between acetylene and formaldehyde in the presence of a catalyst according to Claim 10.
12. 2-butyne-1:4-diol when prepared by the method of Claim 11.

P. L. SPENCER,
Chartered Patent Agent.

PROVISIONAL SPECIFICATION

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- This invention relates to catalysts and more particularly to copper catalysts for the preparation of 2-butyne-1:4-diol.
- 2-butyne-1:4-diol (hereinafter referred to as butynediol) is usually prepared by reacting acetylene with an aqueous solution of formaldehyde in the presence of a catalyst consisting essentially of copper acetylide. The catalyst can be prepared by reacting an aqueous solution of a copper salt with acetylene under appropriate conditions, removing the precipitated copper acetylide and transferring it to the vessel in which the acetylene and the formaldehyde are to be reacted. This procedure may give rise to difficulties in handling the free copper acetylide (which can decompose explosively when dry) and moreover, it has been found that the catalyst particles are liable to attrition during the course of reaction, so that difficulties arise in separating the catalyst and the product liquor.
- To obtain a more robust catalyst, it has been preferred to support the catalyst on a porous solid medium, the procedure being to deposit the copper salt on the support and to convert it to copper acetylide *in situ*. A preferred support has been silica gel and in order to obtain satisfactory catalyst, it has been necessary for the catalyst support to be specially prepared. Catalysts have been described in which the amount of copper held on the support was 10—20% by weight.
- It is an object of the present invention to provide a catalyst much richer in copper than such silica gel-supported catalysts, but which is nevertheless robust and free from the disadvantages of the unsupported catalyst.
- It is a further object of the invention to provide a simplified procedure for the preparation of such a catalyst.
- Yet a further object of the invention is to provide a catalyst which is more efficient on overall considerations.
- According to the present invention, a process for the preparation of a catalyst suitable for use in the reaction between acetylene and formaldehyde comprises as a first stage the preparation of a copper silicate material containing 15—60% by weight of copper, by mixing the requisite proportions of an aqueous solution of a copper salt and a solution of an alkali metal silicate, and separating and drying the precipitate formed, the copper silicate material being subsequently converted to the catalyst by treatment with acetylene.
- The precipitate may be dried by heating in air to temperatures of 100—500° C. or above, or by warming to only slightly elevated temperatures under reduced pressure. On drying, it forms cakes which can readily be broken into granules, but the invention is not limited to

the use of such material. For example, the material may be extruded into rods or other suitable forms. If the material is heated above about 100° C. in the drying process, its colour changes from light blue to black, but catalysts can be prepared from either the blue or the black material.

It is possible, if desired, to impregnate the copper silicate material with further amounts of copper by immersion in a solution of a copper salt and subsequent ignition. In this way, the copper content of the final material can be raised to 60% or more, but this is not essential for the preparation of a useful catalyst.

It is sometimes considered desirable to incorporate in the catalyst for the reaction between acetylene and formaldehyde other materials, generally described as "cuprene inhibitors". A particularly useful example of such inhibitors is bismuth. In carrying out the process of the present invention it is possible to incorporate bismuth or other such inhibitors in the catalyst, either during the first stage of precipitating the copper silicate material or by immersing the dry copper silicate granules in an appropriate solution. It has, however, been found that cuprene formation is greatly reduced when catalysts prepared in accordance with present invention are used as compared with unsupported or silica gel-supported catalysts, and the use of such cuprene inhibitors is accordingly of less importance.

The copper silicate material may be converted into the actual catalyst used in the reaction by suspending it in water and treating with acetylene, the wet material subsequently being transferred to the reactor in which the reaction between acetylene and formaldehyde is to be effected. Alternatively, and preferably, the conversion may be carried out *in situ* in the reactor; in this case, the copper silicate material is added to the aqueous formaldehyde which is warmed above 60° C. and acetylene is then fed to it. The catalyst so prepared is robust. In batch processes in which the catalyst is suspended in aqueous formaldehyde and the latter reacted with acetylene under pressure, the product liquor subsequently being separated from the catalyst which is then re-used, the catalysts of the present invention can be used repeatedly for a large number of successive operations. The separation of product liquor and catalyst remains facile even after much repeated use of the same batch of catalyst. In continuous operation in which aqueous formaldehyde and acetylene are each flowed through a bed of catalyst, catalysts prepared according to the present invention are much less subject to attrition, to dislodgement of copper acetylide, or to blockages causing resistance to flow than are either unsupported copper acetylide or copper acetylide supported on prepared supports.

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F. W. B. KITTEL, M.A. Cantab.,
Chartered Patent Agent.

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